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Chemical Degradation of Castable Refractories in Coal Gasification Process Environments

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National Measurement Laboratory
National Bureau of Standards
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U.S. DEPARTMENT OF COMMERCE, Philip M. Klutznick, *Secretary*

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FOREWORD

Since 1974, the National Bureau of Standards has been engaged in research designed to address materials problems and needs pertinent to coal conversion and utilization technologies. This work, sponsored in part, at first by the Office of Coal Research, then ERDA and currently the DOE, focuses on test method development, particularly accelerated procedures for materials behavior and durability; on the determination of the mechanisms of materials degradation; and on the development and operation of materials data centers to provide evaluated information on properties and performance including failures occurring in operating plants.

During the FY 77-79 period the NBS program, entitled "Materials Research for the Clean Utilization of Coal" consisted of a number of interrelated tasks including:

1. Metal Corrosion
   a. Constant Strain Rate Test
   b. Pre-cracked Fracture Test

2. Ceramic Deformation, Fracture and Erosion

3. Chemical Degradation of Ceramics

   a. Reactions and Transformations
   b. Slag Characterization (viscosity)
   c. Vaporization and Chemical Transport

4. Failure Prevention

   a. Failure Information Center
   b. Materials Properties Data Center

The results of the research have been disseminated through quarterly reports of progress (available from NTIS; report designation EA-6010; Dist. Category UC-90C) as well as numerous scientific publications in technical journals. Further, as individual tasks are completed, an overall report is prepared detailing the results and accomplishments of the project. This present publication is the final report for Task 3 a. Reactions and Transformations.

SAMUEL J. SCHNEIDER
Program Manager
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ABSTRACT

Reactions and transformations that result in chemical degradation of castable refractories used as liners for coal gasification reactors have been studied. In addition to phase analysis of laboratory and pilot plant specimens by conventional x-ray powder diffraction, a new test method was developed that permits changes in the phase composition to be observed without removing the specimen from the test atmosphere. Two candidate castable refractories were included in the study, a high purity $CaO-Al_2O_3$ composition with tabular alumina aggregate (93.7 wt % Al_2O_3, 5.6 wt % CaO) and a $CaO-Al_2O_3-SiO_2$ composition with calcined kaolinite aggregate (55 wt % Al_2O_3, 36 wt % SiO_2, 5 wt % CaO). Specimens were exposed to steam, steam/CO_2, and a simulated coal gasification atmosphere at a pressure of 7 MPa (1000 psig) and temperatures up to 1000 °C. Frequent changes in the bonding phases, and intervals in which a bonding phase was in transition were observed in the case of the high purity castable refractory. The silica-containing refractory, on the other hand, formed bonding phases which were stable in steam over a large range of temperatures and pressures.

CHEMICAL DEGRADATION OF CASTABLE REFRACTORIES IN COAL GASIFICATION PROCESS ENVIRONMENTS

I. OBJECTIVE AND SCOPE OF WORK

Coal gasification processes require the handling and containment of corrosive gases and abrasive particles at high temperatures and pressures. These severe environments cause materials failures which inhibit successful operation and increase costs. The objective of the program at the National Bureau of Standards is to provide test methods and data for evaluating properties of candidate materials under the conditions encountered in coal gasification process plants. The scope of this report is limited to castable refractories for use as liners of reactor vessels. It covers the reactions and transformations that result in chemical degradation when these materials are subjected to typical coal gasification process environments.

II. TECHNICAL APPROACH

Three different approaches have been used at NBS in studying reactions and transformations in candidate refractory castables for gasification reactor liners. The first, or post-exposure approach involved exposure of test bars in hydrothermal pressure vessels, followed by strength tests and x-ray analysis of phase composition after removal from the pressure vessel. A detailed discussion of the correlation of physical properties with phase assemblages observed after exposure is given in the report on Task 2 - Ceramic Deformation, Fracture and Erosion[1]. In addition, some of the earlier results have been summarized in a report by Wiederhorn et al[2].

The second, or *in situ* approach was undertaken because the massive nature of the pressure vessels used for hydrothermal exposure limits the cooling rate so that conditions that prevail at high pressures and high temperatures cannot be effectively quenched. Thus additional reactions and transformations may occur while the specimen is being brought to 25 °C and one atmosphere for testing and examination. It was to eliminate any uncertainty caused by such changes that the decision was made to carry out both the flexural strength measurements and the x-ray analysis *in situ*: that is, without removing the specimen from the chamber. New and highly specialized equipment was designed and built at NBS for this purpose. This report describes the apparatus, method, and results of the *in situ* x-ray analysis. The measurements of flexural strength will be described in a separate report.

The third, or pilot plant exposure approach was based on our examination of approximately forty core samples from the refractory lining of the Conoco Lignite Gasification Pilot Plant in Rapid City, South Dakota. These refractories show the effects of 5.5 years of plant operation, 0.76 years of which were at pressure and temperature (0.9 MPa and 843 °C). The results of characterization of core samples from the Conoco pilot plant by light microscopy, SEM and x-ray powder diffraction have been reported by Dobbyn et al[3]. and have been summarized in a note by Brower et al[4]. Some of the findings will be discussed here in an

attempt to correlate short term *in situ* test data with the effects of much longer exposure under actual service conditions.

Two candidate castable refractories were included in the laboratory study, a high-purity CaO-Al_2O_3 composition with tabular alumina aggregate (NBS A-94) and a CaO-Al_2O_3-SiO_2 composition with calcined kaolinite aggregate (NBS A-56). Samples of CAS_2, CA_2, CA_6 and $C\bar{C}$* were also prepared in order to examine the behavior of these important compounds in more detail. The refractories were cast into bars 75 x 15 x 7.5mm and cured for 24 hours in an environment of 100 percent relative humidity. The bars were then dried at 110 °C for 24 hours and stored in a desiccator for later use in *in situ* testing. Some were fired for five hours at 1010 °C before testing in order to compare the response of fired and unfired specimens to the test atmosphere. Specimens were exposed to steam, steam/CO_2 and to a simulated gasification atmosphere (Table 1) at pressures up to 7 MPa† and temperatures up to 1000 °C. The composition of

Table 1. Nominal composition of the simulated coal gasification atomsphere at approximately 850 °C and 7 MPa.

Component	Amount (Mole %)
CO	20
CO_2	15
H_2	25
H_2O (steam)	40

the atmosphere is difficult to predict if pressure as well as temperature is allowed to vary. It has been our policy to establish the nominal composition shown in Table 1 for a pressure of 7 MPa and to maintain this pressure throughout each series of experiments. Results reported may be assumed to have been obtained at 7 MPa unless otherwise noted. The change in composition with temperature has been examined thermodynamically at NBS by Dr. W. S. Horton. The steam and CO content each increase by roughly 6% while the CO_2 and H_2 content decrease by a similar amount in the temperature range from 600 ° to 1000 °C. The composition shown in the table is, therefore, representative of the middle of the range of experimental conditions covered and deviations from this composition do not exceed ±5%.

*C = CaO, A = Al_2O_3, S = SiO_2, H = H_2O, $\bar{C}$ = CO_2

†The International Standard (SI) unit of pressure is the pascal, or newton per square meter. One mega pascal (MPa) = 10^6 pascals. The conversion to psig is given by p (psig) = (p (MPa) x 145) - 14.7.

III. METHOD AND EQUIPMENT

New and highly specialized equipment was needed in order to obtain x-ray diffraction data without removing the specimen from the pressure vessel. The equipment designed and built at the National Bureau of Standards for this purpose is based on the energy dispersive x-ray diffraction (EDXD) technique described by Giessen and Gordon[5] in 1968.

Unlike conventional diffraction methods, which use monochromatic radiation and a range of diffraction angles, the EDXD method employs white (continuum) radiation and a fixed diffraction angle, 2θ. The diffracted beam is analyzed with a solid state detector and multichannel pulse height analyzer to determine the energy distribution of the photons. Bragg's law in the form given by Sparks and Gedcke[6]

$$E_{hk\ell} = \frac{12.3981}{2 \sin\theta} \cdot \frac{1}{d_{hk\ell}} \qquad (1)$$

is used to calculate the energy E (in kiloelectron volts) of x-ray photons diffracted by planes of spacing $d_{hk\ell}$ (in angstrom units). The channel number, N, is given by

$$N = (E - b)/a \qquad (2)$$

where a and b are calibration constants of the solid state detector system. For the work reported here $\theta = 12.00°$, a = 0.0353 keV/channel, and b = 0.80 keV.

The outstanding advantage of the EDXD method for the present application is that it requires only a single, narrow x-ray path through the pressure vessel. The entrance and exit windows can be as small as a quarter of an inch in diameter, and it is relatively easy to obtain suitable window material in the size and shape required. Using boron carbide, B_4C, it was possible to design for a pressure of 7 MPa with a suitable safety factor while keeping the windows thin enough for adequate transmission of the x-ray beam.

There are sacrifices that must be made as a trade-off for the speed and convenience of the EDXD method. The most serious is the low resolution of the detector, which results in peaks that are more than an order of magnitude wider than in conventional diffractometry.

Details of the construction of the pressure vessel are shown in Figure 1. The upper view is a section through the vessel in the plane of diffraction. Radiation from the x-ray source (A) passes through a 1/8 inch thick window of boron carbide (B) and, after being scattered by the specimen (C), passes through a second window (B) and slit (D) to enter the solid state detector (E). The bracket (F) which supports the specimen has slots milled in it for the x-ray beam. These limit the divergence of the incident and diffracted beams to 2 °. An internal heater consisting of an alumina core (G) wound with approximately 6 feet of 0.032 inch diameter 80% Pt-20% Rh wire (H) surrounds the specimen

bar. A concentric alumina tube (I) is wrapped with platinum foil (J) to reduce heat transfer by radiation. The heater assembly is mounted in a U-shaped bracket of 0.031 inch thick Inconel sheet (M) which forms three sides of a box. The remaining three sides are formed by a cover (L) of 0.010 inch thick Inconel. The space between the heater and the box is packed with fibrous alumina insulation. Internal windows of 0.002 inch thick mica mounted in platinum disks (N) loosely cover the ends of the heater core to reduce convection currents while allowing the x-ray beam to pass. The importance of these disks should not be underestimated, as operating temperatures without them are limited to about 500 °C. Three thermocouples are provided. The first (O) is attached to the front edge of the specimen at the top. The second (P) is at the bottom of the vessel where it senses the temperature of the water that collects there. The third (not shown) is on the outside of the vessel in contact with the belt heater (not shown) that surrounds the vessel. Coned pressure fittings in ports (Q) and (R) are used to connect the gauge assembly and the water reservoir.

The pressure vessel, which is machined from 316L stainless steel, is 4 1/2 inch in o.d. at the height of the x-ray beam and has 1/2 inch thick walls. The flange is 6 inches in diameter. Twelve 3/8-16 high-tensile-strength bolts are used to attach the lid, which is fitted with a gold-plated K-shaped flange seal made of Inconel X-750. The enclosed volume is approximately 435 ml. The side arms, which contain the x-ray windows, are also made of 316L stainless steel and are welded in place at an angle corresponding to $2\theta=24$ °. The boron carbide windows are sealed with gold plated V-gaskets of Inconel X-750. As the windows appeared somewhat grainy even after they were polished, the surfaces in contact with the gaskets were sputtered with gold to fill any irregularities and provide a softer seat. Threaded caps compress the gaskets and support the load due to gas pressure.

In operation, the pressure vessel is mounted as shown in Figure 2. A base assembly supports both the pressure vessel and the solid state detector and provides the necessary adjustments for alignment. This base is pivoted at a point directly below the focal spot of the x-ray tube for ease in setting the take-off angle. Three leveling screws are used for setting the height and for making small adjustments to the angle of incidence. The base supports a heavy ring 8 1/4 inches in diameter in which the pressure vessel is clamped by four 3/8 inch radial set screws, the ends of which extend into holes in the six inch flange of the vessel. In addition to supporting the pressure vessel the mounting ring provides a means for counteracting the force applied in tightening the lid bolts. There are 12 3/8 inch holes drilled vertically through the ring. A 10 inch lever is attached by means of pins that fit any diametrical pair of holes. Equal and opposite forces applied to this lever and the wrench provide the necessary torque to tighten the bolts without disturbing the alignment of the instrument.

Since the vessel must often be operated with its walls at temperatures as high as 285 °C in order to maintain a steam pressure of 7 MPa, it is equipped with an external belt heater visible just below the x-ray

ports in Figure 2. While heating the vessel, it is important to minimize the heat transferred to the base, the detector, and the x-ray tube. With this aim, the i.d. of the mounting ring was made 1/4 inch greater than the o.d. of the vessel flange. The four set screws comprise the only path for the conduction of heat from the vessel to the mount. A heavy copper sheet with a 1/8 inch aperture is mounted between the exit slit and the detector window to aid in the dissipation of heat that might otherwise be transferred to the detector. The only direct link between the vessel and the x-ray tube is a stainless steel beam tunnel that fits inside the safety shutter. Although this tunnel has thick walls (to reduce x-ray leakage) heat transfer to the x-ray tube has not been a problem.

External fittings visible in Figure 2 include the gauge block assembly and the water reservoir. The gauge block provides, in addition to the gauge, a pressure tubing connection for introducing gases, a needle valve, and a rupture disk. The water reservoir has a capacity of 40 ml. It is pressurized with nitrogen gas to ensure that water will flow into the pressure vessel when the needle valve is opened.

The lid of the pressure vessel is fitted with two pressure seal assemblies for electrical leads, one for the four thermocouple leads, and the other for a single power lead rated at 40 amperes. The vessel itself serves as the conductor for the grounded side of the low voltage power supply of the internal heater.

A safety shield of 1/4 inch thick steel is installed before the vessel is pressurized. A portion of this shield can be seen behind the pressure vessel in Figure 2. The enclosure is connected to an exhaust system in case of leakage of test atmospheres containing CO, H_2, or H_2S.

After installing the specimen bar with the thermocouple attached, an initial charge of 20 ml of water is added to the vessel before closing the lid. Approximately 15 ml would be required to pressurize the vessel with saturated steam at 7 MPa. Excess liquid remains at the bottom of the vessel and its temperature is controlled by means of the external heater to maintain the desired partial pressure of steam. Other components of the atmosphere are added as gases to obtain the desired total pressure. A reserve supply of water is kept in the 40 ml reservoir to replenish any used in hydrating the sample or lost during the run.

The wall temperature required to maintain a steam pressure of 7 MPa is approximately 285 °C. The external belt heater has a rating of 650 watts at 240 V ac, but the power input during steady-state operation does not exceed 400 watts.

Specimen temperature is separately controlled using the internal heater. The maximum current required for control at 1000 °C in steam is 14 amperes, corresponding to a power input of 390 watts. As the power input to the internal heater is increased, that to the external heater

must be reduced to compensate. A small blower has been installed in case additional cooling is required. It is not generally needed.

Specimen temperature is usually increased in increments of 50 °C. Diffraction patterns are recorded after 6 hours, and again after 24 hours. A series of experiments covering the range to 1000 °C and 7 MPa requires from 3 to 6 weeks.

Reference patterns of known phases occurring in refractory cements are needed in order to recognize these phases when they are encountered in the course of an experiment. Since energy dispersive x-ray diffraction patterns differ considerably from those prepared with a conventional diffractometer, a special set of reference standards had to be prepared. Actually two sets of standards were prepared, one by obtaining samples of the desired material and recording the pattern with the EDXD apparatus, and the other by calculating the pattern from data given in standard references such as the Powder Diffraction File[7]. An example of an actual EDXD pattern for α-quartz is given in Figure 3. Calculated patterns are given for AH, AH_3, C_3AH_6, $C_4A_3H_3$, and $C\bar{C}$ (Figure 4), for α-A, CA_6, CA_2, CA, C_3A and β-A (Figure 5), and for α-S_Q (quartz), S_C (cristobalite), A_3S_2 (mullite) and low CAS_2 (Figure 6). In addition to being compact and convenient to reproduce, the computed patterns have the advantage that a tabulation identifying all of the lines is available. When a peak is composed of a number of unresolved lines, the components are clearly shown in the computed pattern.

Computer methods used to assist in the interpretation of the sixty or more EDXD patterns resulting from each test included (1) automatic plotting of the patterns on a common axis system for ease in comparison, (2) subtraction of corresponding ordinates and plotting of the difference to show subtle changes, and (3) plotting of the intensity of selected lines for a series of patterns recorded over a range of pressure and temperatures. Examples will be included in section IV - RESULTS AND CONCLUSIONS.

IV. RESULTS AND CONCLUSIONS

The approximate bulk compositions of the castable refractories NBS A-94 and NBS A-56 are shown by squares on the phase diagram of the system $CaO-Al_2O_3-SiO_2$[3] (Figure 7). The chemical analyses are given in Table 2.

Table 2. Chemical analyses (dried basis) of castable refractories (weight percent)

	NBS A-94	NBS A-56
Al_2O_3	93.7	55.
CaO	5.6	5.
SiO_2	0.1	36.
Fe_2O_3	0.3	1.3
Others and loss on ignition	0.3	2.7

In general, the *in situ* experiments were designed to monitor the behavior of an unfired castable during its initial heating, during exposure at 1000 °C and 7 MPa and during the cooling down phase of the cycle. Specimens were examined before and after exposure tests by conventional x-ray powder diffractometry. A list of the compounds observed is given in Table 3. Some are metastable, others such as the calcium aluminates may contain H_2O (although shown here as anhydrous), and several of the hydrated calcium aluminates may be non-stoichiometric with respect to H_2O.

Table 3. Compounds encountered in exposure studies of A-94 and A-56

C_3A	C_2AH_8	β-C_2S	α-A
$C_{12}A_7$	CAH_{10}	C_8S_5	β-A_{ss}
CA	C_3AH_6		
CA_2	$C_4A_3H_3$	C_2AS	AH
CA_6		CAS_2 (2 forms)	AH_3
C_4A_3	$C\overline{C}$		
	CH	S_c, S_q	A_3S_2

C = CaO, A = Al_2O_3, S = SiO_2(S_q quartz or S_c cristobalite) H = H_2O, $\overline{C}$ = CO_2

Steam is usually the chemically dominant component of the test atmosphere, as shown by the response of refractories to simulated or actual gasification environments. In the experiments described below the total pressure was maintained at 7 MPa, the design limit for our apparatus, except for a few cases when the test temperature was so low that the equilibrium vapor pressure of water was too low to sustain the

desired pressure. This condition occurred below 285 °C for the steam atmosphere or 230 °C for the simulated gasification environment. The estimated total pressure is given only when it is lower than 7 MPa.

A-94 Exposure Tests

The composition of A-94 is represented by a square on the join CaO-Al_2O_3 of the CaO-Al_2O_3-SiO_2 phase diagram (Figure 7). The compound assemblage commonly observed in cast and dried (but unfired) test bars includes: CA, CA_2, α-A, CAH_{10}, C_2AH_8, C_3AH_6, and AH_3. The aggregate is tabular alumina.

With increasing temperature, the A-94 refractory passes through a sequence of phase assemblages consisting of hydrated calcium aluminates, hydrated aluminates, and α-A. The sequence observed in steam, with approximate equilibrium dissociation temperatures, is

$$CAH_{10}+AH_3 \xrightarrow{20°C} C_3AH_6+AH_3 \xrightarrow{110°C} C_3AH_6+AH \xrightarrow{240°C} C_4A_3H_3+AH \xrightarrow{345°C} C_4A_3H_3+A \xrightarrow{625°C} CA_2+A$$

in general agreement with the pseudobinary diagram of Crowley for the system CaO-Al_2O_3-H_2O at 100 MPa[9]. Above about 625 °C none of the hydrated phases is stable. At this point CA_2 forms as the bonding phase, and the assemblage CA_2, α-A (with a trace of β-A) is observed in all tests up to 1000 °C. The reactions are reversible and have been followed by the *in situ* method. The bonding phases C_3AH_6 and AH_3 dissociate over a rather narrow temperature interval compared with $C_4A_3H_3$ and AH. C_3AH_6 forms readily in saturated water vapor at ∿ 93 °C and dissociates at ∿ 240 °C and 3.3 MPa. $C_4A_3H_3$, which forms above ∿ 240 °C and 3.3 MPa, persists to ∿ 625 °C. It is the most difficult phase in the system to monitor by the EDXD method because of the weak and poorly resolved x-ray pattern.

AH (boehmite) has been shown in NBS work under Task 2, Ceramic Deformation, Fracture and Erosion, to be one of the most important phases in the high purity castable refractory A-94. The observed loss of flexural strength of this refractory has been correlated with the decomposition of this compound. The "equilibrium" dissociation temperature of AH is ∿ 345 °C. However, with rising temperature, this dissociation was repeatedly observed to occur over a range of ∿ 200 °C. Small amounts of AH are commonly present at ∿ 500 °C. The compound decomposes rapidly above 500 °C, and a refractory containing appreciable amounts of the hydrate should not be heated rapidly through this temperature region.

The ability of the *in situ* method to follow the dissociation of AH in real time is shown by the series of four x-ray patterns reproduced in Figure 8. The overall change is shown in a difference plot, Figure 9, in which the negative peaks correspond to the AH phase consumed in the reaction, while the positive peaks show the increase in α-A, the reaction product.

Physical properties, such as strength and erosion resistance, which are affected by the presence of AH, can be expected to follow trends somewhat parallel to the formation or dissociation of this phase. For example, the flexural strength of the test bar used in this series of experiments might be expected to show the same trend as the intensity of the x-ray pattern of the AH phase.

In Figure 10 the intensity of the 251 reflection of AH (channel 610) and the intensity of the 116 reflection of α-A (channel 492) have been plotted for a sequence of fourteen experiments covering the range from 247 °C and 3.2 MPa to 650 °C and 4.1 MPa in steam. There was a substantial loss of AH during 21 hours at 375 °C and 3.8 MPa (experiment 8) and at each subsequent temperature - pressure increment up to 650 °C and 4.1 MPa (experiment 14). Under the conditions of these experiments the flexural strength of the test bar would be expected to decrease at temperatures from 375 °C to 650 °C at ∿ 4 MPa in steam.

In steam/CO_2, or in the simulated gasification environment, formation of hydrated calcium aluminates may be suppressed by the reaction of CaO with CO_2 to form $CaCO_3$. This compound dissociates in the presence of steam at ∿ 700 °C, which is generally above the stability range of the hydrated phase.

Addition of dissolved silica to a test atmosphere of high pressure steam results in formation of a reaction rim ∿ 1mm thick formed on test bars of high purity A-94. The reaction rim was composed mainly of C_2AS, β-CS, CA_2, and α-A. Formation of hydrated calcium aluminates was thus inhibited. Since silica impurities in coal would be expected to contribute dissolved silica to the pressurized steam of a gasification reactor, similar reactions between dissolved silica and an initially high purity calcium aluminate castable can be expected to occur.

A-56 Exposure Tests

As may be seen from Figure 7, the composition of A-56 lies in the compatibility triangle A_3S_2 (mullite) - CAS_2 (anorthite) - S (quartz, tridymite or cristobalite). The phase assemblage of the as-cast test bars is quite complex. Hydrated compounds such as AH, AH_3, CAH_{10}, C_2AH_8 and C_3AH_6 are commonly present as minor phases in addition to the anydrous major phases S_c, A_3S_2, CA and CA_2. As the temperature is raised, in the presence of steam or the gasification atmosphere, hydrated phases gradually dissociate. The dominant reaction is in the main, a hydrothermal one, with high pressure steam interacting with CA, CA_2, α-A and S_c to form the very strong bonding phase CAS_2 (anorthite) and the stable assemblage CAS_2, A_3S_2, S. This assemblage is subject to leaching in an open system such as a gasification reactor. Loss of SiO_2 to the high pressure steam is commonly observed in the *in situ* experiments. The dissolved silica is usually precipitated as cristobalite, or a mixture of cristobalite and quartz depending on temperature and time of cooling.

Only the triclinic form of CAS_2 was observed in the *in situ* studies, but a hexagonal (metastable) form was observed in some of the post-exposure studies of the Ceramic Deformation and Erosion specimens (Task 2) and in some of the Conoco refractories. This phase may form hydrothermally, by crystallization from high-temperature melts in air, and by solid state reactions. It rapidly transforms to triclinic CAS_2 in the presence of steam below 700 °C[10].

For NBS A-56 and several commercial $CaO-Al_2O_3-SiO_2$ castables studied, there is a passage from complex to much simpler phase assemblages with rising temperature in high pressure environments containing steam. By a variety of paths and reactions, the composition produces the stable assemblage A_3S_2, S, CAS_2 previously referred to in Figure 7. The formation of new compounds at the expense of others is primarily a function of temperature at 7MPa. Alumina gels, α-A, CA, CA_2, and the various hydrated calcium aluminates react with S_c to form the bonding phase CAS_2. CAS_2 was observed forming in the 350-550 ° temperature range and more rapidly at 700 ° - 1000 °C.

Compared with the unfired test bars, those fired in air at 1010 °C for 20 hours show a large increase in CA_2, a slight increase in A_3S_2, the presence of poorly crystallized C_2AS and CAS_2, a decrease in α-A and S_c, and the absence of hydrated forms. As before, with exposure to the hydrothermal environment at 7 MPa this assemblage is changed to CAS_2, A_3S_2 and S with silica in the cristobalite form. The flexural strength of the castable is markedly increased as these reactions progress in the gasification atmosphere.

Two supplementary experiments with test bars near CAS_2 in composition were conducted in a steam atmosphere. The unfired bars consisted initially of CA, CA_2 and silica, with an excess of A. After casting, the bars were composed of SiO_2 (quartz form), α-A, CA, and AH_3. X-ray analysis gave no indication of a gel phase. Exposure times were 168 and 330 hours. In both series of experiments, some hydration and subsequent dehydration of free alumina as well as the dissolution of free silica was observed as temperatures and steam pressures were increased. Formation of hydrated calcium aluminates was not observed. At approximately 160 °C and 0.5 MPa $Ca_8Si_5O_{18}$, a phase not previously encountered in these studies, was formed in preference to hexagonal or triclinic CAS_2. According to Speakman et al.[11] $Ca_8Si_5O_{18}$ is metastable, and of variable composition. The compound, along with free silica, persisted to 525 °C. In the temperature interval 525-625 °C, $Ca_8Si_5O_{18}$ dissociated and/or reacted with the SiO_2 to form triclinic CAS_2. This is shown in the *in situ* x-ray pattern of Figure 11 (a), (b), and (c). Pattern (a) is of the unfired test bar at 25 °C and ambient pressures. Pattern (b) was recorded at 520 °C and 7 MPa steam and shows the presence of well developed Ca_8S_5 as indicated by two prominent diagnostic peaks. Pattern (c) was obtained one hour later after the temperature had been raised to 625 °C and 7 MPa steam. It shows that at this temperature, most of the Ca_8S_5 had dissociated/decomposed, releasing CaO for the formation of CAS_2. The presence of $Ca_8Si_5O_{18}$ suppresses the formation of CAS_2 by incorporating available Ca. Its occurrence in a refractory would appear to be undesirable.

Conoco Pilot Plant Samples

In addition to the *in situ* tests of A-56, results of exposure of two similar commercial refractories to service conditions in the Conoco Lignite Gasification Pilot Plant are available. Approximately 40 core samples were examined by optical microscopy, SEM, and x-ray powder diffractometry. The following generalizations are based on the examination of the Conoco samples as well as on the *in situ* tests.

1) The atmosphere of a coal gasification reactor is a complex mixture of gases. Steam is the dominant component of this mixture as shown by chemical and structural changes in the CaO-Al_2O_3-SiO_2 refractory.

2) A hydrothermal reaction in which SiO_2 in the form of cristobalite (S_c) progressively reacts with free α-A, A_3S_2 and the calcium aluminate binder (CA, CA_2) to form the bonding phase CAS_2 (anorthite) is seen to be the dominant reaction in laboratory and pilot plant studies.

3) Pilot plant specimens show a loss of SiO_2 from the calcined kaolin aggregate (reaction rims). Some of the silica reacts to form CAS_2. At $\sim$ 900 °C some silica reacts with free α-A to form A_3S_2, and some is lost from the refractory, precipitating in regions of lower temperature as cristobalite or a mixture of cristobalite and quartz. The latter was frequently observed in the *in situ* tests.

4) Evidence of the apparent fluxing action of alkalies, resulting in surface melting at the working face of the refractories and the formation of a residual crust $\sim$ 2-3mm in thickness was observed. Alkali reaction with the refractories was also shown by the presence of $(Na_{1.5}K_{0.5})Al_2Si_2O_8$ (Nepheline, idealized formula) near the hot or working face of refractory specimens from the pilot plant.

5) The formation of hexagonal CAS_2 was not observed in the *in situ* x-ray studies, but was obtained hydrothermally in work of the NBS Fracture and Deformation Task group in selected high pressure experiments. The compound may be formed by cooling from the melt, by solid state reactions, or hydrothermally. It is considered to be a metastable form and transforms rapidly below 700 °C in the presence of steam to the triclinic form. It should be noted that the 700 °C region would represent a temperature interval in which the primary bonding phase of the refractory is in a state of transition. The hexagonal form of CAS_2 was observed as a minor phase in a number of specimens of pilot plant refractories taken 3 to 6 inches from the working face of the castable.

6) As previously described, when reactions in test bars approximating the composition CAS_2 (composed of CA, CA_2, and S in the form of powdered quartz) were monitored by the *in situ* x-ray method, the metastable compound C_8S_5 was observed to form quite rapidly at 160 °C and 0.5 MPa. Formation of this compound suppressed the formation of CAS_2 by incorporating the available calcia. C_8S_5 dissociates at ∿ 525-625 °C at 7 MPa and CAS_2 then forms readily. In this temperature interval, a refractory might well suffer a loss of strength; the formation of C_8S_5 appears to be undesirable. Its presence has not been observed in our work with other $CaO-Al_2O_3-SiO_2$ castables, even when quartz has been used as a source of silica. Its formation appears to be favored by the ready availability of all three components of CAS_2.

7) It is difficult to estimate the effect of leaching by a gasification environment on the CAS_2 and A_3S_2 components of a $CaO-Al_2O_3-SiO_2$ castable. However, available data suggest that refractories of this type are a desirable choice for the working face of a gasification reactor lining. As mentioned previously, bonding phase CAS_2 develops rapidly in the temperature interval 700-900 °C in the presence of steam. Free α-A reacts at 900-1000 °C to form A_3S_2. Once formed, CAS_2 persists when cooled from operating to ambient conditions of temperature and pressure.

Summary

The *in situ* x-ray studies have shown that, in the presence of steam and with changes in temperature, a high purity castable refractory is subjected to frequent changes in bonding phases and to intervals in which the main bonding phase is in a state of transition. These changes are undesirable and should be minimized by avoiding exposure of the refractories to steam below 750 °C, or preferably 900 °C. Reaction of the high purity refractory with steam containing alkalis and silica from impurities in the coal should be expected to occur at the working face with formation of various silicates. These may alter the course of hydration/dehydration reactions and the formation of bonding phases.

The $CaO-Al_2O_3-SiO_2$ refractory has been shown (Task 2) to increase markedly in flexural strength with exposure to either simulated or pilot plant gasification atmospheres. The increase in strength is attributed to the formation of CAS_2 and A_3S_2. Once formed, these compounds are not subject to hydration/dehydration and are stable in steam over a large temperature range. Leaching of silica and other components from this type of refractory has been observed, but may not pose a serious problem during the service life of the material.

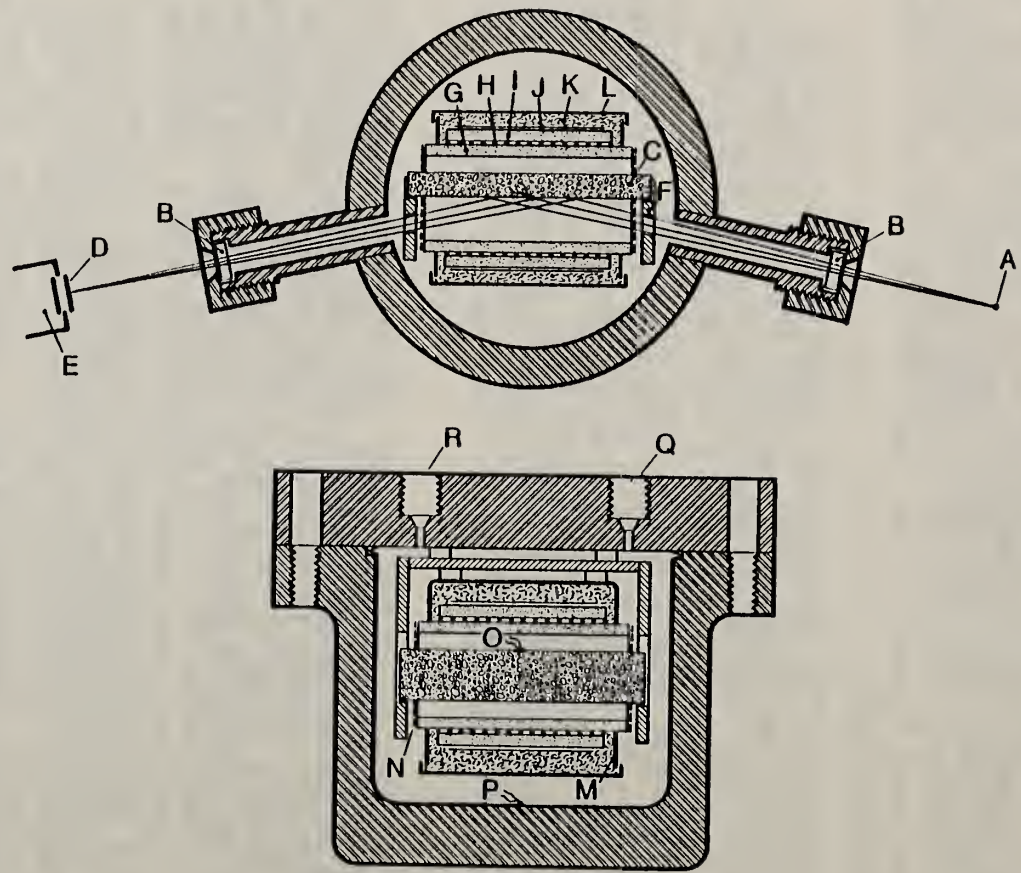

Figure 1. Assembly drawing of the x-ray pressure vessel showing: (A) x-ray source, (B) B_4C windows, (C) specimen, (D) receiving slit (E) solid state detector, (F) specimen mounting bracket and divergence slits, (G) heater core, (H) heater winding, (I) insulating cover, (J) heater sheath, (K) insulation, (L) heater case, (M) heater support bracket, (N) mica windows, (O) specimen thermocouple, (P) bottom thermocouple, (Q) port for pressure gauge assembly, and (R) port for water reservoir.

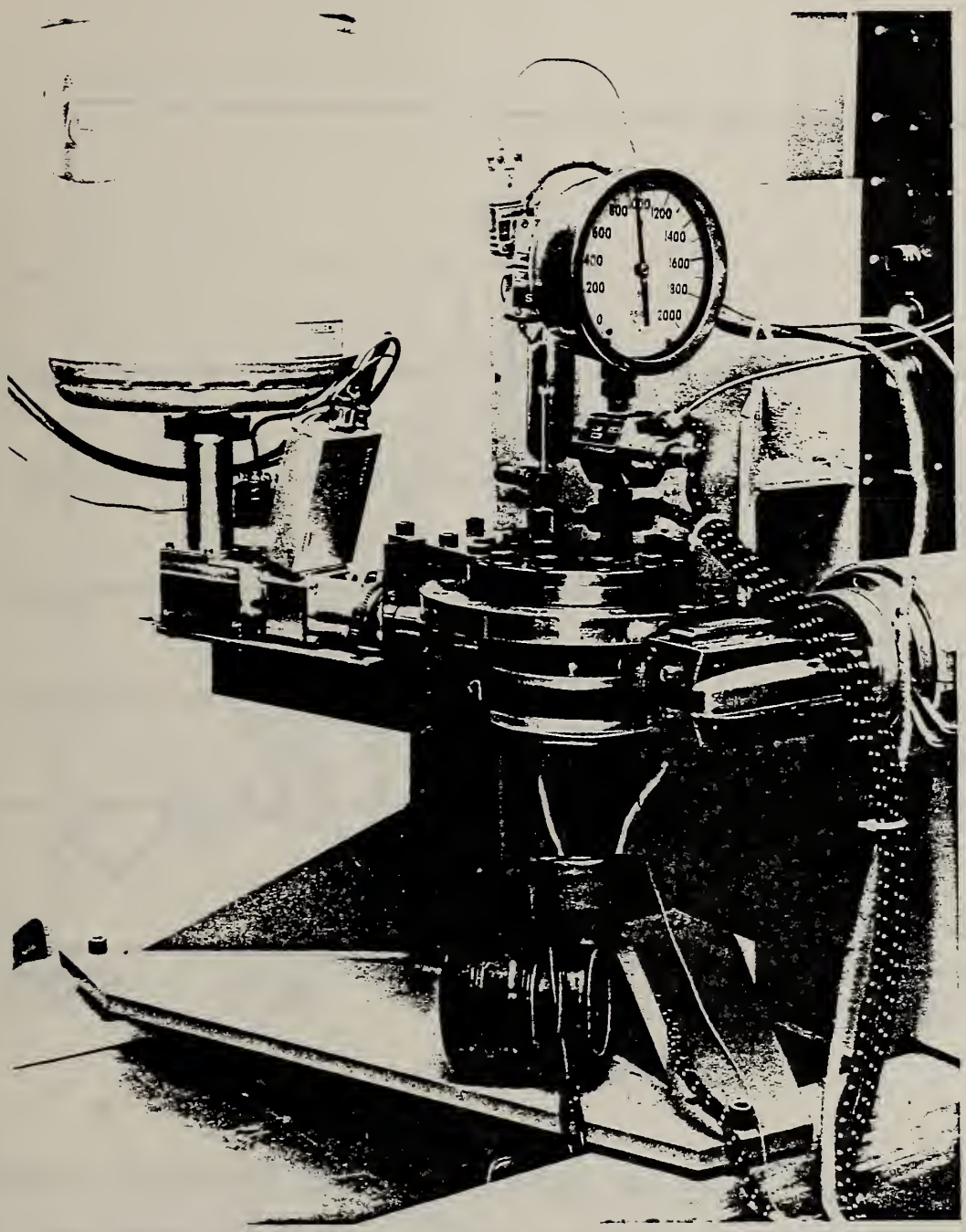

Figure 2. The pressure vessel and solid state detector mounted at the x-ray tube.

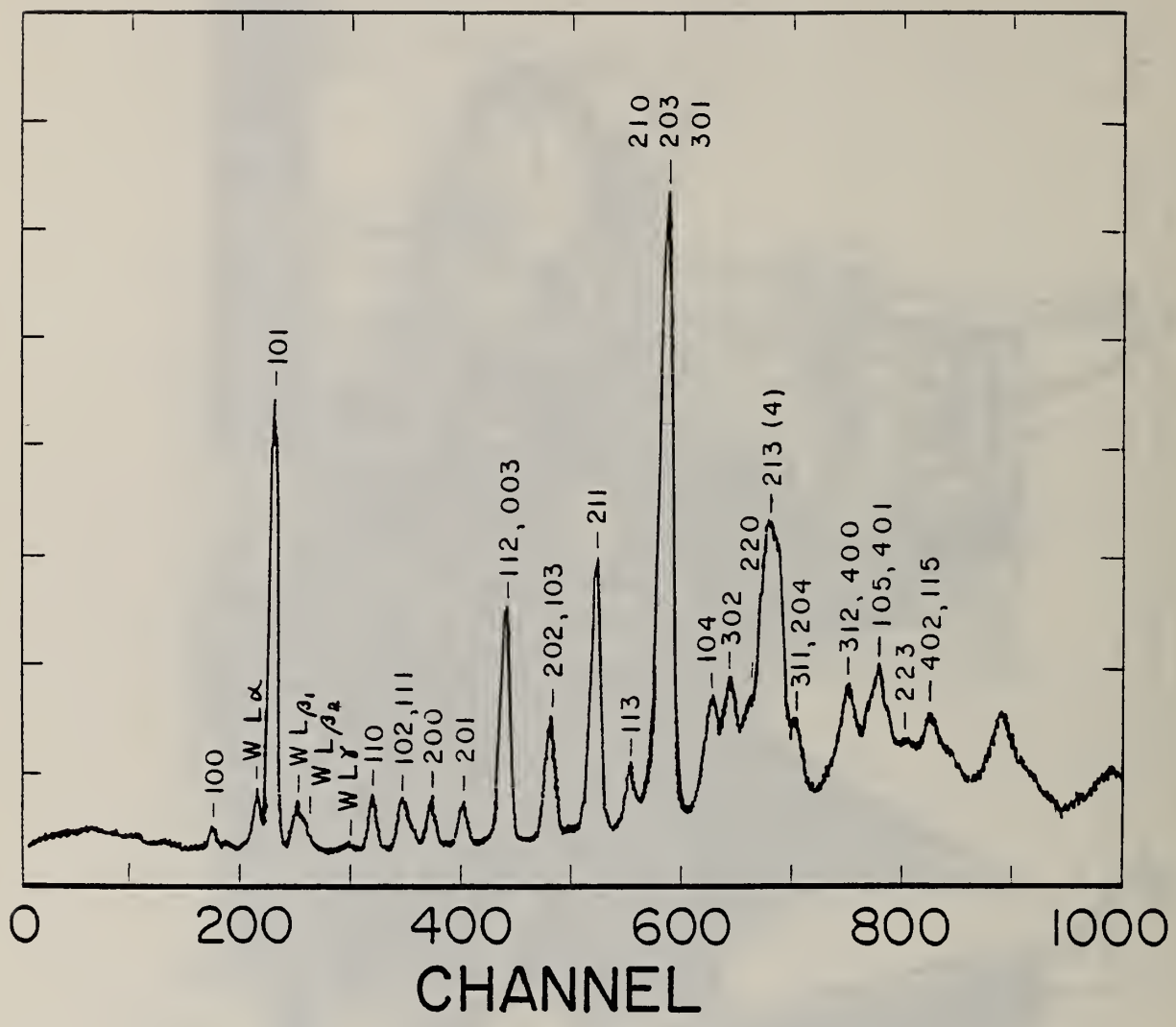

Figure 3. EDXD pattern of α-quartz (SiO_2). Diffraction peaks are identified by their Miller indices. Four lines from the characteristic spectrum of the tungsten x-ray tube are also identified (W Lα; W $L\beta_1$, W $L\beta_2$ and W Lγ).

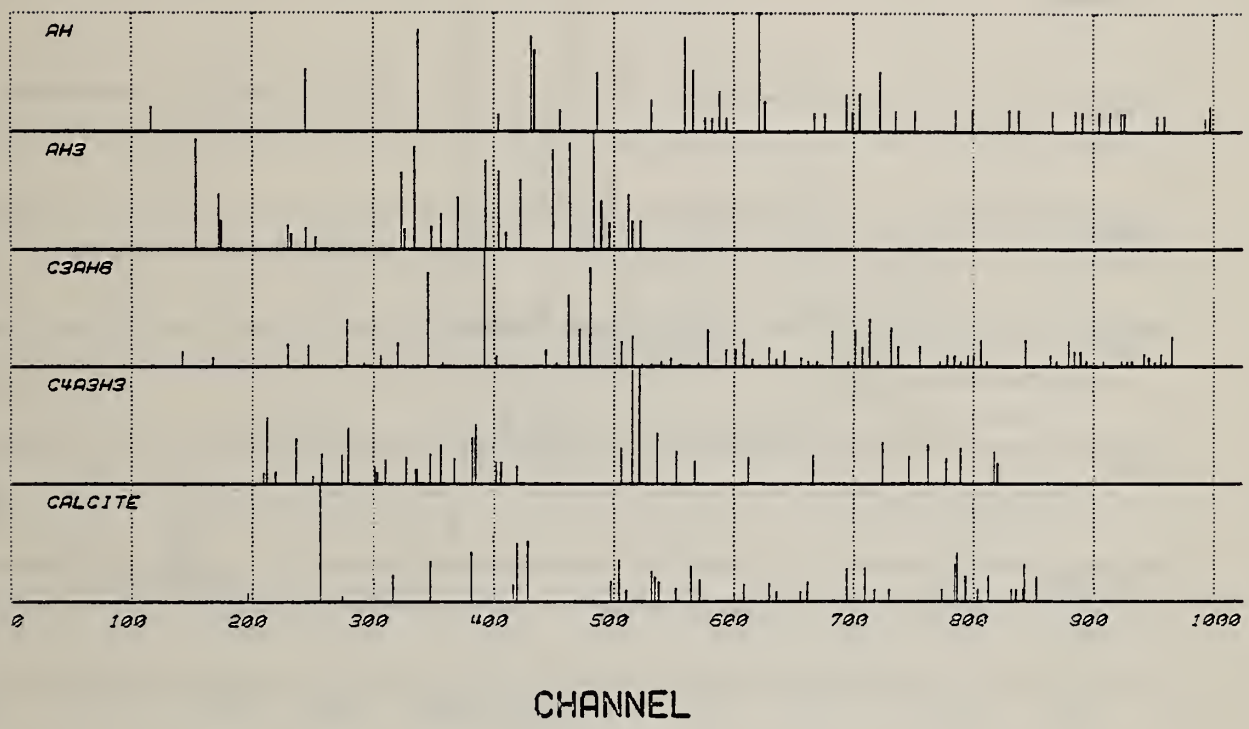

Figure 4. Calculated EDXD patterns of AH, AH_3, C_3AH_6, $C_4A_3H_3$, and $C\overline{C}$.

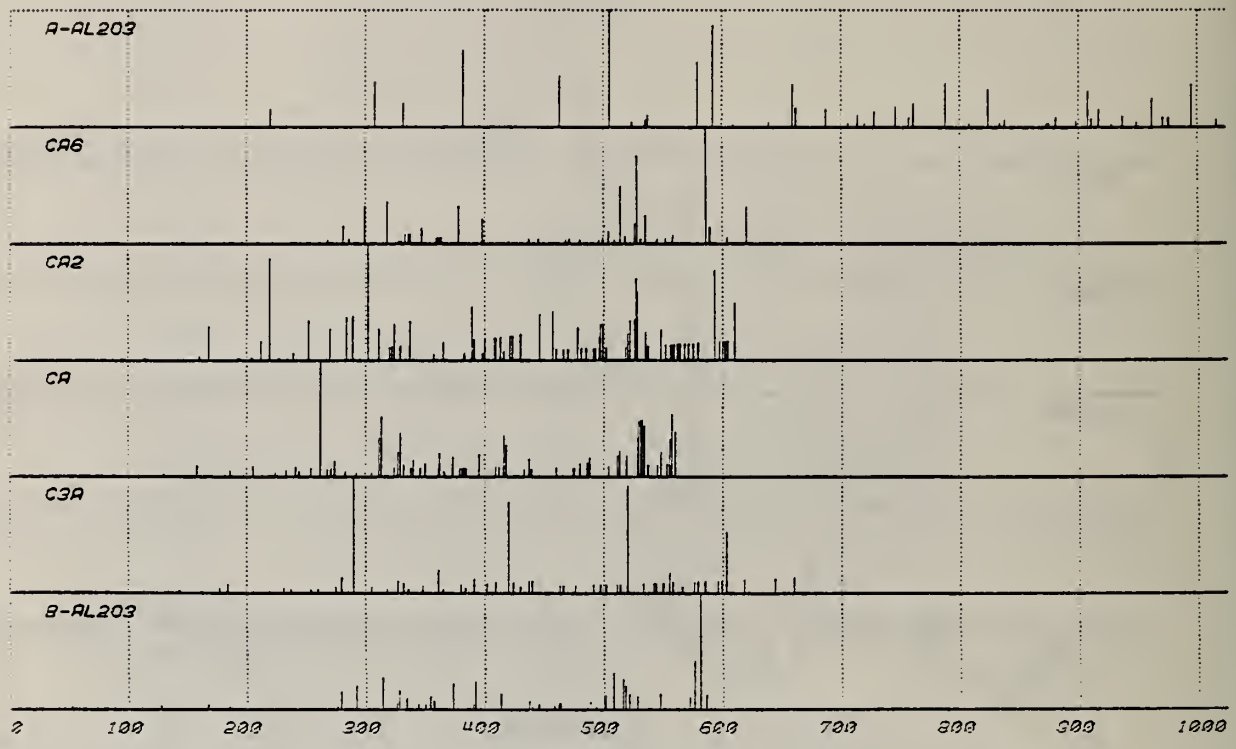

Figure 5. Calculated EDXD patterns of α-A, CA_6, CA_2, CA, C_3A, and β-A.

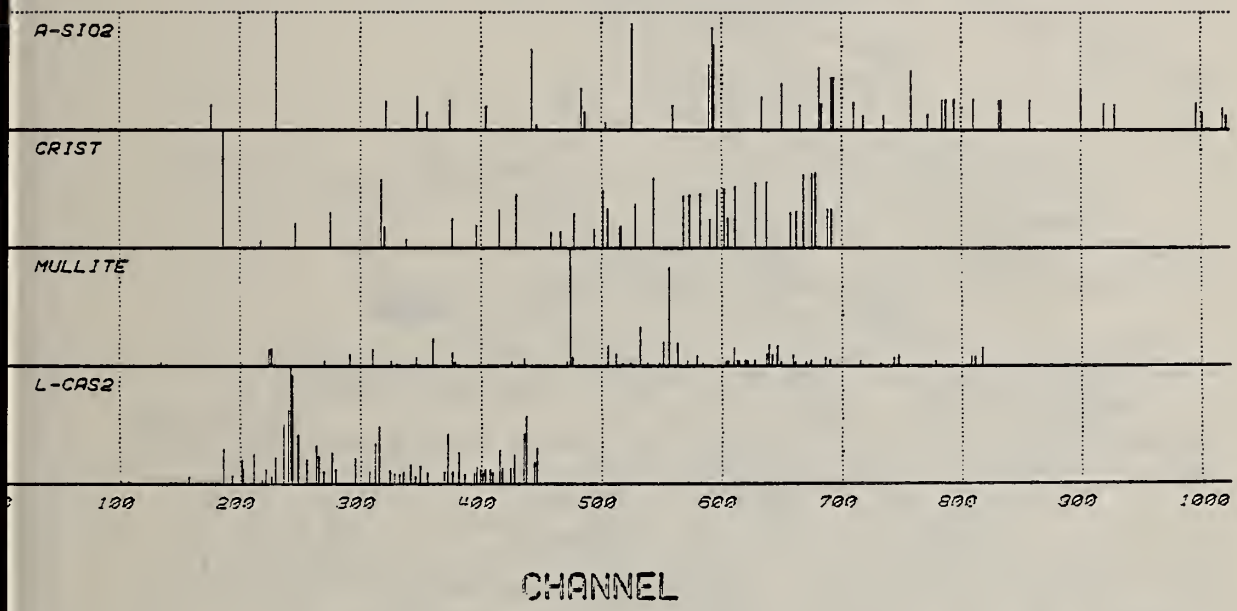

Figure 6. Calculated EDXD patterns of α-S_q (quartz), S_c (cristobalite), A_3S_2 (mullite), and low CAS_2.

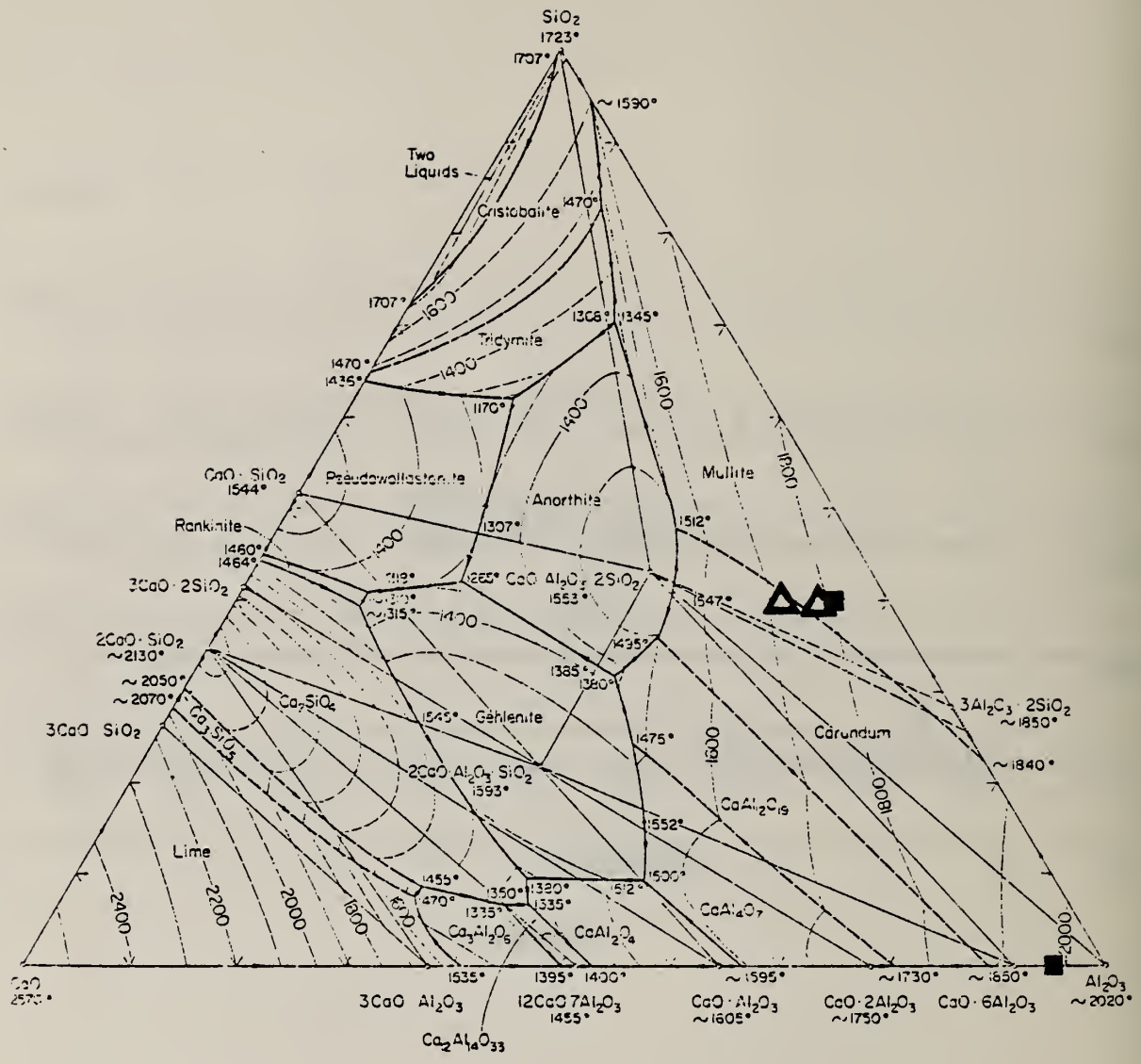

Figure 7. Phase diagram of the system $CaO-Al_2O_3-SiO_2$ showing the compositions of NBS castable refractories (solid squares). A-56 lies in the compatibility triangle $A_3S_2-CAS_2-S$, while A-94 is on the join $CaO-Al_2O_3$. The compositions of two commercial refractories used in the Conoco pilot plant are represented by open triangles.

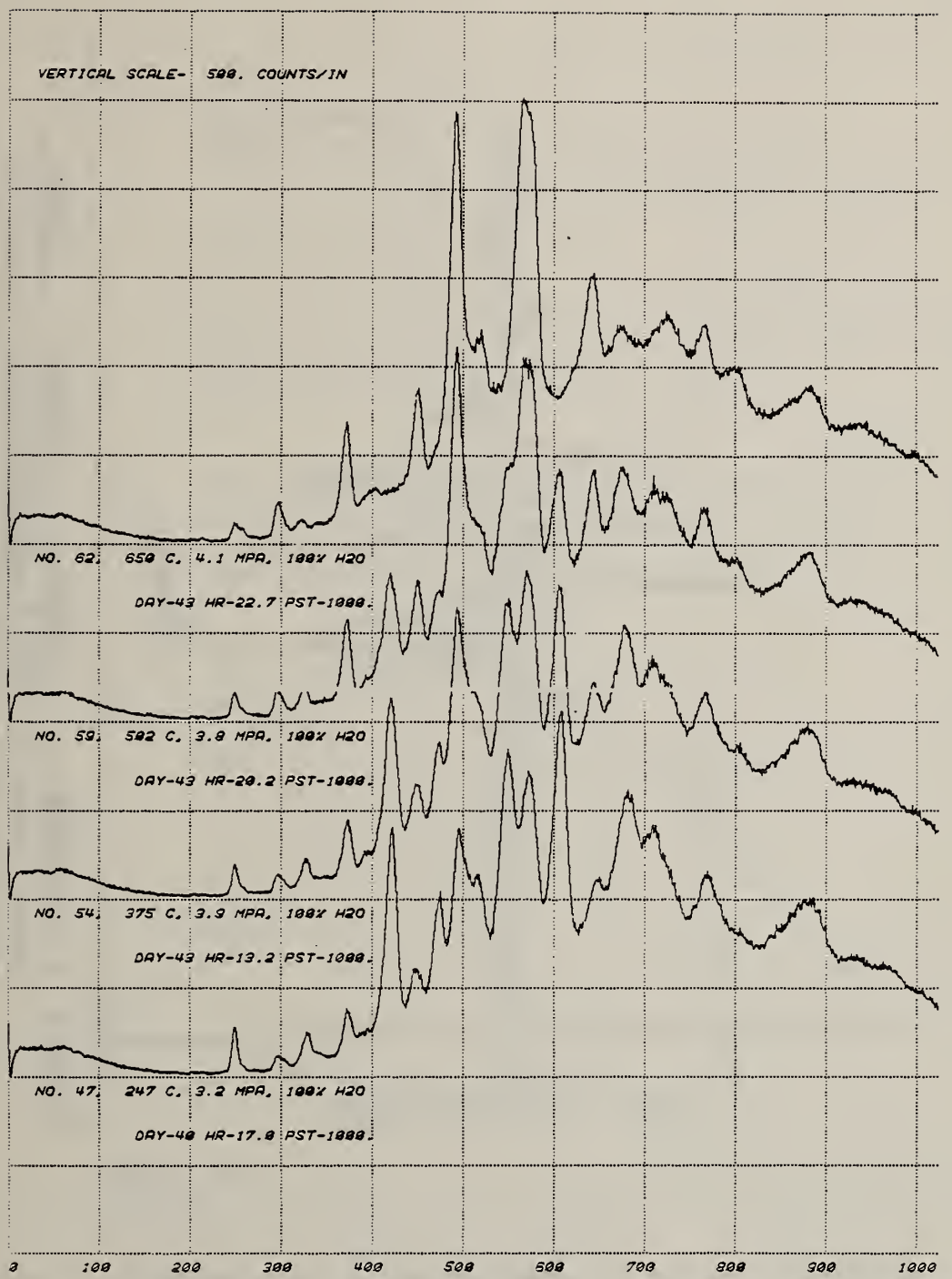

Figure 8. A series of four EDXD patterns showing the dissociation of AH (boehmite) and the formation of additional α-A in the range from 247 °C and 3.2 MPa to 650 °C and 4.1 MPa.

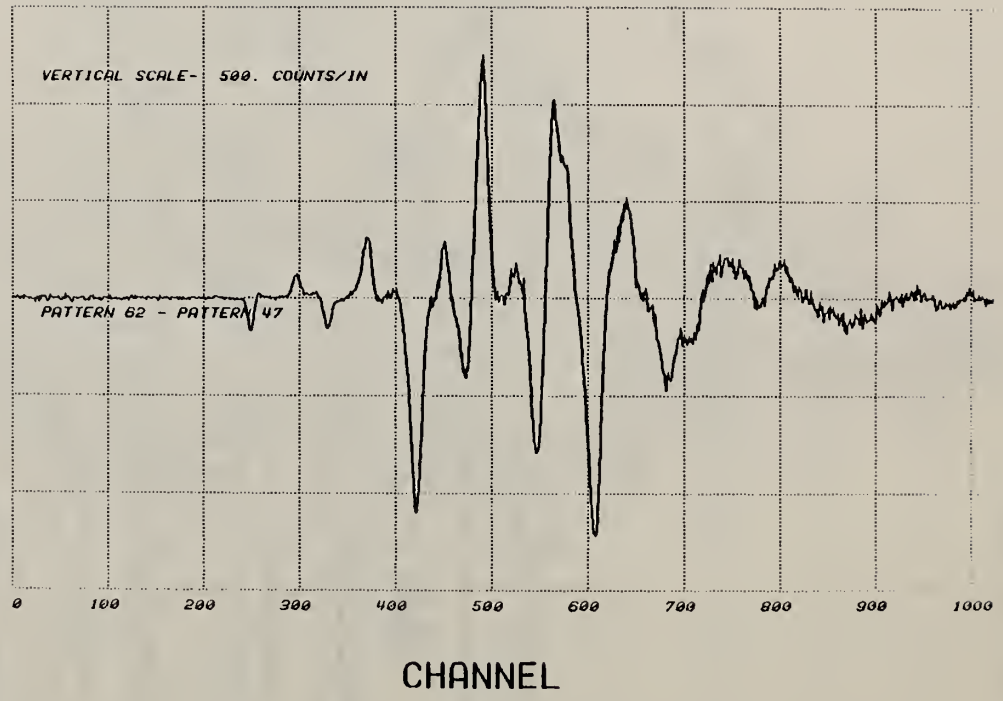

Figure 9. A difference plot (pattern 62 - pattern 47) showing the overall change in phase composition in the temperature range from 247 °C to 650 °C at approximately 3 to 4 MPa in steam. The negative peaks correspond to the AH phase consumed in the reaction, while the positive peaks show the increase in the concentration of α-A, the reaction product.

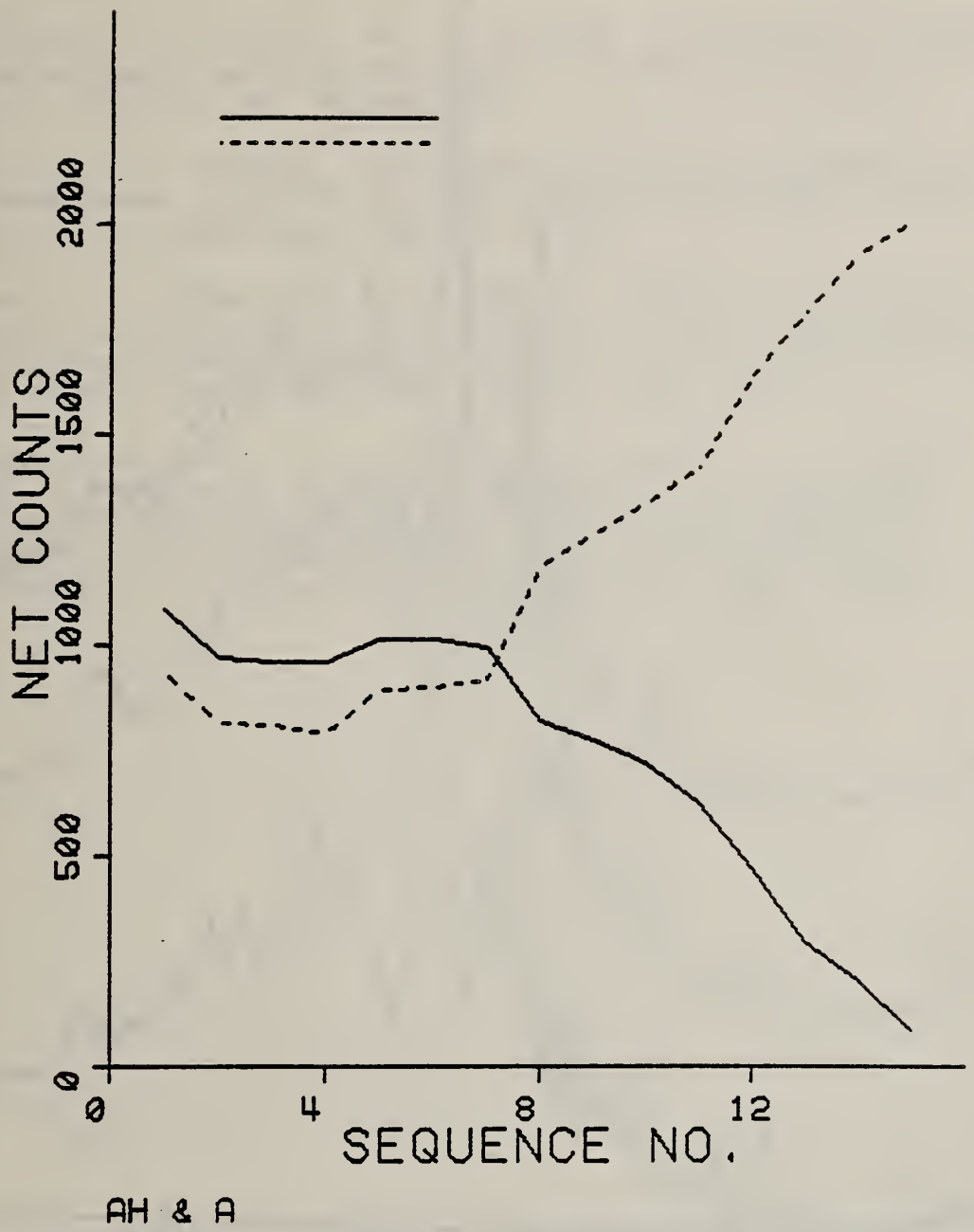

Figure 10. Computer plot of the intensity of the 251 reflection of AH (solid line) and the 116 reflection of α-A (dashed line) for a sequence of fourteen experiments. The dehydration of AH is evident in the temperature range from 375 °C to 650 °C at a pressure of approximately 4 MPa.

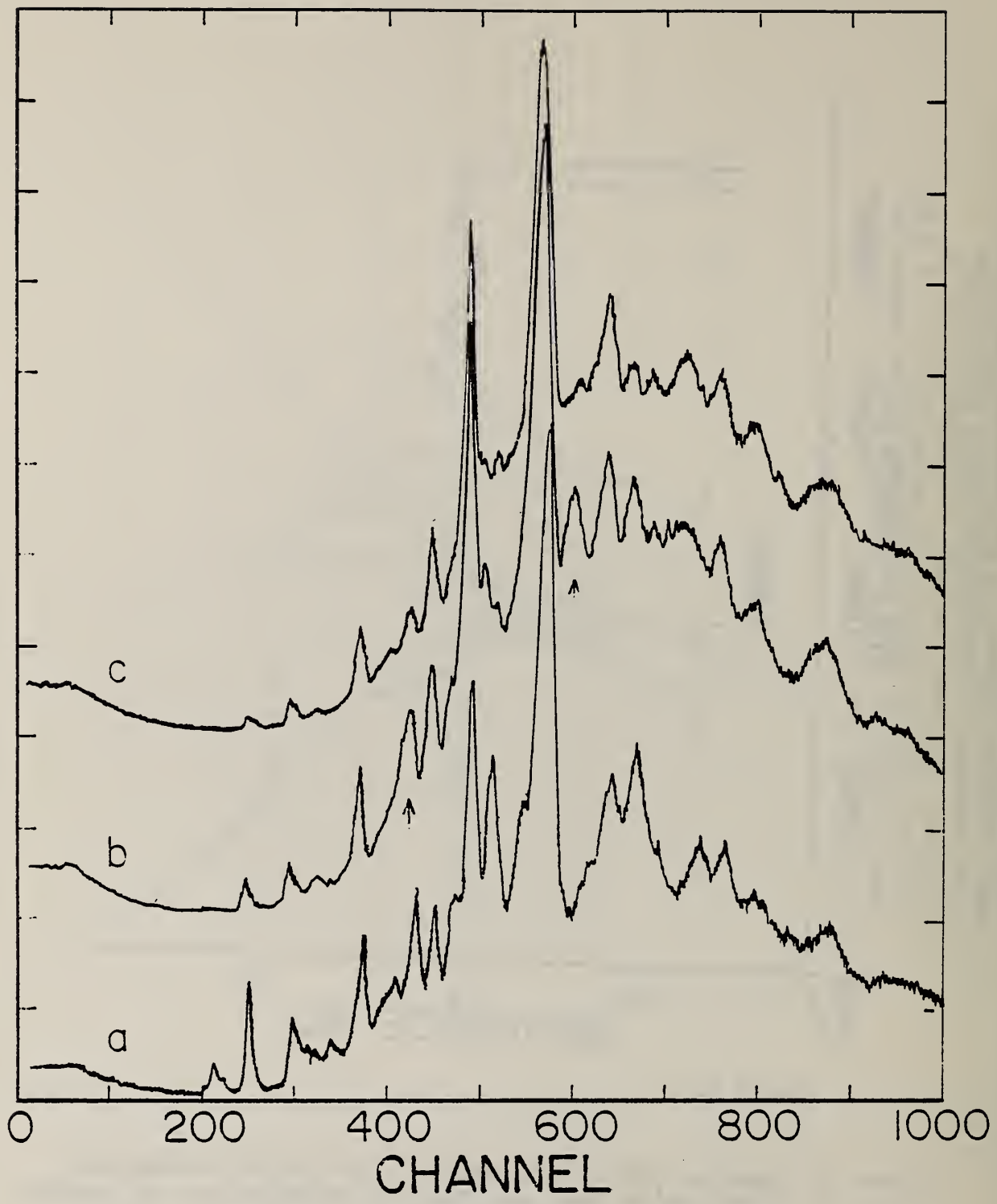

Figure 11. EDXD patterns of an unfired test bar of CAS_2 (a) at 25 °C, (b) at 520 °C and 7 MPa steam, and (c) at 625 °C and 7 MPa steam one hour later. Two lines of the C_8S_5 phase are identified with arrows.

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16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

Reactions and transformations that result in chemical degradation of castable refractories used as liners for coal gasification reactors have been studied. In addition to phase analysis of laboratory and pilot plant specimens by conventional x-ray powder diffraction, a new test method was developed that permits changes in the phase composition to be observed without removing the specimen from the test atmosphere. Two candidate castable refractories were included in the study, a high purity CaO-Al_2O_3 composition with tabular alumina aggregate (93.7 wt % Al_2O_3, 5.6 wt % CaO) and a CaO-Al_2O_3-SiO_2 composition with calcined kaolinite aggregate (55 wt % Al_2O_3, 36 wt % SiO_2, 5 wt % CaO). Specimens were exposed to steam, steam/CO_2, and a simulated coal gasification atmosphere at a pressure of 7 MPa (1000 psig) and temperatures up to 1000 °C. Frequent changes in the bonding phases, and intervals in which a bonding phase was in transition were observed in the case of the high purity castable refractory. The silica-containing refractory, on the other hand, formed bonding phases which were stable in steam over a large range of temperatures and pressures.

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